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NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

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SYNTHESIS OF SOME ANALOGUES OF 1,1-BIS-(*p*-CHLOROPHENYL)-2,2,2-TRICHLOROETHANE (DDT)

I. THREE FLUORINE ANALOGUES[1]

BY S. KIRKWOOD[2] AND J. R. DACEY[3]

Abstract

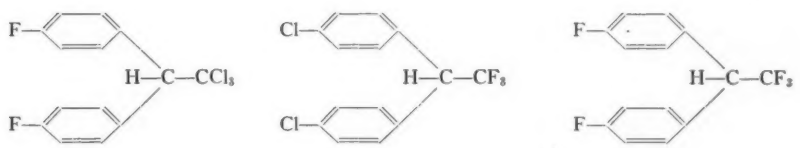
The compounds 1,1-bis-(*p*-fluorophenyl)-2,2,2-trichloroethane, 1,1-bis-(*p*-chlorophenyl)-2,2,2-trifluoroethane, and 1,1-bis-(*p*-fluorophenyl)-2,2,2-trifluoroethane have been prepared, and their method of preparation is outlined. The toxicity of these compounds to *Drosophila melanogaster* supports Läuger's hypothesis of the mechanism of the action of DDT.

Introduction

The great efficiency of the compound 1,1-bis-(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) as an insecticide makes it desirable to synthesize analogous molecules and determine their potency as insecticides. In this manner some knowledge may be obtained of the structural features of the DDT molecule responsible for its great toxicity; further, any useful and interesting tendencies towards a species specificity in any of the analogous molecules may be noted.

Experimental

The following compounds were prepared as outlined below.



I II III

1,1-Bis-(p-fluorophenyl)-2,2,2-trichloroethane (I)

This compound was prepared by carrying out the Baeyer condensation using chloral and fluorobenzene (5). Fluorobenzene is conveniently prepared using Flood's adaptation of the Schiemann reaction (1).

[1] *Manuscript received November 14, 1945.*

Contribution from the Chemical Warfare Laboratories, Department of National Defence (Army), Ottawa, Canada.

[2] *Lieutenant, Canadian Army.*

[3] *Major, Canadian Army.*

Chloral hydrate (69.5 gm., 0.42 moles) was dissolved in 400 ml. of concentrated sulphuric acid contained in a three-necked flask. While the solution was kept under vigorous agitation with a propellor type stirrer, 80 gm. (0.84 moles) of fluorobenzene was added and the temperature controlled at 45° C. Sixty millilitres of 20% fuming sulphuric acid was added during the course of the reaction. After two hours the acid mixture was poured over ice and the fluoro compound extracted with ether. The ether was washed twice with water and dried with sodium sulphate. After removal of the ether the compound was distilled under reduced pressure.

The product was a colourless viscous liquid that crystallized on standing and had a characteristic odour. Yield, 90 gm. (67%); b.p., 153° C. (at approx. 6 mm.); m.p., 41° to 42° C. corr. Calc. for $C_{14}H_9Cl_3F_2$: Cl, 33.2; F, 11.82%. Found: Cl, 33.97, 34.41; F, 11.91, 11.77%.

1,1-Bis-(p-chlorophenyl)-2,2,2-trifluoroethane (II)

This compound was prepared by the fluorination of DDT using Henne's method (3).

DDT (40 gm., 0.11 moles) was placed in a large platinum dish and thoroughly mixed with 54.4 gm. (0.25 moles) of mercuric oxide. The dish was placed in a good hood and an excess of liquid hydrogen fluoride was added. The mixture was stirred and the dish set aside until the excess hydrogen fluoride had evaporated. It was then poured over ice, and the water suspension filtered through a layer of filtercel on a Büchner funnel. The material on the funnel was thoroughly washed with water and then the organic materials were washed through with boiling ethanol. On diluting the ethanol with water a low melting crystalline solid separated out. Twenty-seven grams of material was obtained which melted over the range 45° to 50° C. and which was apparently a mixture of mono-, di-, and trifluoro DDT.

These fluoro compounds were quite difficult to separate by recrystallization, their solubilities being apparently very similar. Methyl alcohol was found to be the best solvent; the material was therefore recrystallized from it by dry-ice–acetone cooling. Five such recrystallizations resulted in a yield of 8.5 gm. of a white nicely crystalline compound with a characteristic odour. The melting point was sharp and could not be raised by further recrystallization; m.p., 64° to 65° C. corr. Calc. for $C_{14}H_9Cl_2F_3$: Cl, 23.3; F, 18.69%. Found: Cl, 22.94, 23.19; F, 18.52, 18.71%.

1,1-Bis-(p-fluorophenyl)-2,2,2-trifluoroethane (III)

This compound was prepared by the fluorination of 1,1-bis-(*p*-fluorophenyl)-2,2,2-trichloroethane (I). Thirty grams (0.94 moles) of (I) was placed in a platinum dish and thoroughly mixed with 46·8 gm. (0.22 moles) of mercuric oxide. The mixture was treated with hydrogen fluoride and worked up in the same manner as Compound (II). The product was a mixture of 17 gm. of white crystalline fluorides, which melted over the range 70° to 80° C. Repeated recrystallization from methanol using dry-ice–acetone cooling brought it up to a constant melting point. The result was a white

nicely crystalline compound with a characteristic odour; m.p., 79° to 80° C. Calc. for $C_{14}H_9F_5$: Cl, 0.00; F, 34.92%. Found: Cl, 0.87, 0.75; F, 34.75, 34.88%.

It was desirable to know with certainty the extent to which fluorination had taken place in Compounds (II) and (III), there being no guarantee that all three chlorines on carbon atom No. 2 of the ethane nucleus could be replaced by Henne's technique. Since carbon and hydrogen determinations in organic compounds containing fluorine are often unreliable, it was decided that a direct determination of both chlorine and fluorine would give a more accurate measure of the extent to which fluorination had occurred. The chlorine analysis by the Carius method was quite satisfactory, the high solubility of silver fluoride preventing it from interfering. The method of McCombie and Saunders* was used to determine the fluorine content. The results using this method were quite satisfactory and establish the extent of fluorination beyond doubt.

These compounds were submitted to the Department of Genetics of McGill University for an assay of their potency as insecticides. The test insect was *Drosophila melanogaster*. The results were as follows:

Compound	Potency
I	2/5 that of pure DDT
II	1/100 that of pure DDT
III	1/100 that of pure DDT

Discussion

Läuger *et al.* (4) have given a summary of the investigations carried out by the J. R. Geigy Company that led to the discovery of the insecticidal powers of the DDT molecule. He postulates that the extreme toxicity of DDT is due to the basic toxicity of the *p*-bridged 4,4′-dichlorodiphenyl structure, coupled with the augmenting effect of the chloroform residue. The *p*-bridged 4,4′-dichlorodiphenyl structure probably acts by an enzyme-blocking mechanism while the chloroform residue, he claims, acts as a lipophilic group, which causes the molecule to have an affinity for the nerve lipoids. In order to test this hypothesis a number of molecules were synthesized which possessed the same 1,1-(*p*-chlorophenyl)ethane structure as DDT but which had residues corresponding to inhalation anaesthetics other than chloroform. All the molecules possessed insecticidal activity and their activity varied roughly as the partition coefficient of the anaesthetic whose residue was used to replace that of chloroform. Thus there seems to be some justification for Läuger's hypothesis of the mechanism of the action of DDT.

In order to carry these studies further, the above compounds were synthesized. On the basis of Läuger's hypothesis, (II) and (III) at least should be inactive, since fluoroform has no anaesthetic or other physiological effects when inhaled (2).

* *Private communication.*

As would be expected from Läuger's hypothesis, (II) and (III) have little or no activity. What activity they do possess may well be due to slight contamination by the parent compounds from which they were made, i.e., DDT and (I). Since both of these compounds are extremely active, even traces would show activity at 100 times the concentration of pure DDT.

Acknowledgment

Acknowledgment is made to McGill University for assistance in having the biological assay made, and to Dr. Léo Marion of the National Research Council, whose laboratory carried out the micro-Carius determinations.

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FLOW–PRESSURE RELATIONS IN CALCIUM-SOAP–OIL SYSTEMS[1]

WILFRED GALLAY[2] AND IRA E. PUDDINGTON[3]

Abstract

Flow–pressure relations have been determined for suspensions of calcium soaps in mineral oils of varying viscosity and viscosity index. The effect of small amounts of reagents on the character of these curves is very marked. The addition of water generally increases the yield value of the system without affecting the mobility, while solvents for calcium soaps tend to change the mobility without altering the yield value.

Introduction

Flow–pressure curves in two-phase systems rarely follow the predictions of Poiseuille's equation and they usually show some type of anomalous flow. It is to be expected that the flow properties of lyophobic suspensions will be influenced by any interaction between the solid particles as well as by the volume they occupy. If the particles are completely independent of one another and are of such a shape that close packing may be obtained, dilatancy will probably result. If, however, the solid particles attract one another and form aggregates, a definite amount of pressure may have to be applied to cause flow. In such cases yield values will be found.

Since it has been shown (3, 4) that small amounts of addition agents sometimes have a large effect on the degree of flocculation of certain dispersions in organic media, viscometric measurements on these systems become of interest. The present communication deals with the results obtained when the viscosities of calcium-soap–mineral-oil dispersions were measured. Systems of this type form one of the larger groups of lubricants in use to-day, viz., the calcium base lubricating greases, and a knowledge of their flow properties becomes of obvious commercial interest.

Experimental

A laboratory-made viscometer of the Stormer type, shown diagrammatically in Fig. 1, with a rotating paddle and a stator fitted with baffles, was used in this work. The stator, although rigidly clamped in place during a determination, could be rotated by means of a motor to provide mechanical stirring of the mix. An air thermostat about the rotor and stator gave adequate temperature control. Flow–pressure curves were obtained by plotting the rate of fall of the basket against the load in the basket. The true viscosity of the system is then represented by the slope of the curve, and the yield value

[1] *Manuscript received November 5, 1945.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1380.

[2] *Formerly, Chemist, National Research Laboratories; now, Consulting Chemist, Ottawa, Canada.*

[3] *Chemist.*

by the intercept on the pressure axis. Experiment showed that a load of 3 gm. was required to turn the rotor with the stator empty, and this value should be used as a blank in examining the graphs.

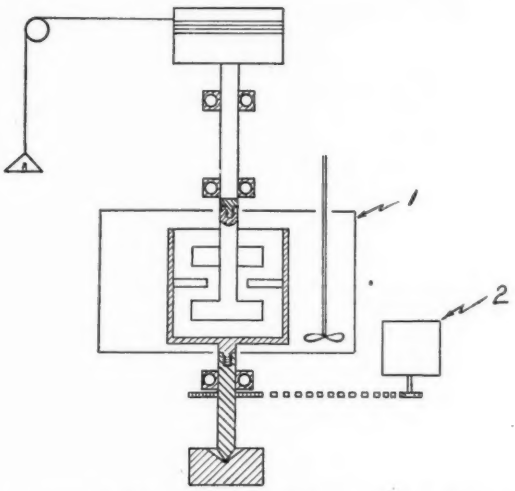

FIG. 1. *Diagram of viscometer: 1, air thermostat; 2, stirring motor.*

Fig. 2 shows the results obtained with this instrument using three mineral oils of different viscosities. Curves 1, 2, and 3 represent flow–pressure relations for oils having viscosities of 5000, 2000 and 300 Saybolt Universal Seconds at 100° F.

Viscosities were determined on suspensions of calcium soaps, with and without addition agents, in mineral oils that varied both in viscosity and viscosity index. Most of the measurements were made at room temperature since it was found that the results obtained here were substantially the same as those found at higher temperatures. Some of the more noteworthy results are shown graphically in the next section.

Results

Calcium Stearate

The results reported here were obtained with City Chemical Company pure calcium stearate.

In order to determine the effect of stirring on the flow properties of calcium-stearate–oil dispersions, measurements were made at various time intervals after the dispersions were made up. Fig. 3 shows the results obtained with a 40% suspension of calcium stearate in an oil with a viscosity of 150 S.U.S. at 100° F. and a viscosity index of 70. The points for Curves 1, 2, 3, 4, 5, and 6 were found after 0, 10, 20, 30, 90, and 190 min. of stirring, respectively. Curve 7 shows the effect of adding 1.5% of a soap solvent (citral) and Curve 8

gives the result when 5% of water, based on the soap, is added. It is immediately seen that the soap solvent has virtually no effect on the flow properties of the dispersion, while water changed the yield value markedly without altering the mobility of the material.

Changes in the flow properties with increasing dispersion are sufficiently small after 30 min. of stirring to have little effect on subsequent measure-

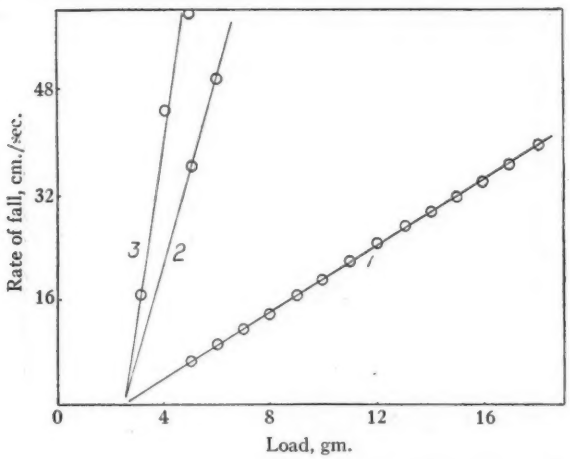

FIG. 2. *Flow–pressure curves for liquids: 1, 2, and 3 represent results obtained with mineral oils with viscosities of 5000, 2000, and 300 S.U.S. at 100° F., respectively.*

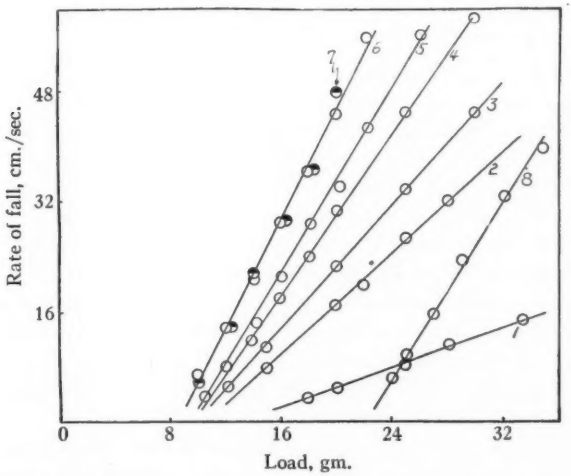

FIG. 3. *Flow–pressure curves for calcium-stearate–oil suspensions: 1, 2, 3 4, 5, and 6 taken after 0, 10, 20, 30, 90, and 190 min. of stirring; 7, after the addition of 1.5% of citral; 8, after addition of 5% of water.*

ments, and the procedure of stirring each new sample for 30 min. and an additional 10 min. for each portion of addition agent added, before measurements were taken, was adopted.

The effect of increasing amounts of water is shown in Fig. 4, where Curves 1, 2, 3, and 4 represent the result of additions of 0.0, 1.1, 2.7, and 6.7% of water (based on the soap) to a suspension of 30% of calcium stearate in a mineral oil with a viscosity of 150 S.U.S. at 100° F. and a viscosity index of 70.

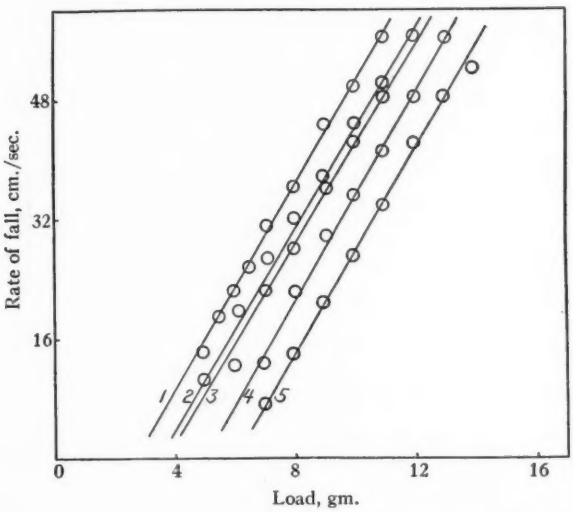

FIG. 4. *Flow–pressure curves for calcium-stearate–oil suspensions: 1, 2, 3, and 4 taken after addition of 0.0, 1.1, 2.7, and 6.7% of water; 5, same composition as 4, taken after standing overnight.*

Further additions of water up to 13.4% did not change the flow properties. After standing overnight the yield value increased as shown by Curve 5. Here again the addition of water has changed the yield value only.

Additions of glycerol to these systems produce results similar to those yielded by water but the effect is considerably less. The effect of free stearic acid is intermediate between that of water and glycerol.

Fig. 5 shows the effect of changing the concentration of soap while the soap-to-water ratio remains constant. Curves 1, 2, 3, 4, and 5 illustrate the changes in flow properties when a commercial calcium soap grease was diluted with 0, 10, 35, 50, and 70% of oil. The effect is substantially a change in yield value only with each addition of oil.

The results at elevated temperatures appear to vary only in degree from those obtained at room temperature. Measurements taken without water in the vicinity of 100° C., where the soap is swollen, show an increased viscosity but no yield value. The addition of water to such a system causes a

decrease in viscosity and a marked increase in yield value. On cooling, the yield value is still further increased. The decrease in viscosity is probably due to the coagulative effect of the water. With fatty acid, however, the

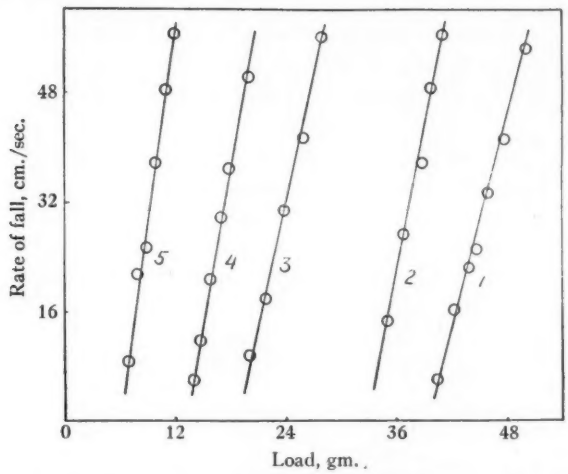

FIG. 5. *Flow–pressure curves for calcium-soap–oil suspensions: 1, 2, 3, 4, and 5, curves for commercial lubricating grease after the addition of 0, 10, 35, 50, and 70% of oil.*

picture is somewhat different. Initial additions bring about an increased swelling of the soap particles and cause the system to form a more homogeneous mass. With further additions of fatty acid the viscosity reaches a maximum and then decreases as the soap goes into true solution. The yield value in all cases is very small.

Table I summarizes the effect of the addition of water and fatty acid to dispersions of calcium stearate in oils with viscosities of 300 S.U.S. at 100° F. and viscosity indices varying from 25 to 95. Changes in viscosity of the oil change the slope of the flow–pressure curve but do not influence the yield value. The effect of addition agents is somewhat reduced as the viscosity of the oil is increased, however. The results shown in the table were obtained at room temperature.

Some general observations may be made from these results. The true viscosities of the soap–oil suspensions decrease slightly with increase in the viscosity index of the oil. The addition of water or fatty acid has little effect on this property. The initial yield value is slightly greater if the oil has a viscosity index above 70, and this difference is greatly accentuated by the addition of water. Changes in the yield value due to the addition of fatty acid increase somewhat with increasing viscosity index of the oil. The flow properties of dispersions of calcium stearate in mineral oils with viscosity indices of 70 and 95 are virtually identical provided the viscosities are the same.

TABLE I

THE EFFECT OF ADDITION AGENTS ON THE FLOW PROPERTIES OF CALCIUM STEARATE DISPERSIONS

V.I. of oil	Slope of curve				
	Initial slope	After addition of water	After addition of fatty acid	Change due to water	Change due to fatty acid
25	1.51	1.73	1.86	0.22	0.35
40	1.80	1.97	2.03	0.17	0.23
70	2.33	2.41	1.95	0.08	−0.38
95	2.31	2.41	2.18	0.10	−0.13
V.I. of oil	Yield value				
	Initial yield value	After addition of water	After addition of fatty acid	Change due to water	Change due to fatty acid
25	8.7	8.8	11.5	0.1	2.8
40	8.7	10.5	15.0	1.8	4.5
70	11.3	25.2	15.0	13.9	3.7
95	11.7	25.8	17.7	14.1	6.0

The most outstanding result in these data is the increase in yield value with decreasing polarity of the suspending medium (increase in V.I.) and the accentuation of this property by the addition of water. Since it has been shown previously (4) that small amounts of water have a marked influence on the surface properties and equilibrium sedimentation volume of calcium stearate in oil, this is not unexpected. Highest yield values usually occur where the degree of flocculation of the solid material is greatest, and this condition, as shown by sedimentation experiments, is found with polar solids, where the polarity of the medium is least. The work of von Buzagh (1), who noted quantitatively that the force of adhesion between solid particles suspended in liquid media varied in the same order as the sedimentation volume of the solid, is in agreement with this.

Calcium Oleate Dispersions in Mineral Oils

Since preliminary experiments with a commercial calcium oleate showed it to be unsuitable, the soap used for this work was prepared by neutralizing U.S.P. grade oleic acid with potassium hydroxide in alcoholic solution and reacting the product with an aqueous solution of calcium acetate. After washing, the product was dried at 105° C. and ground to about 200 mesh.

A 40% suspension of this material in a mineral oil with a viscosity of 300 S.U.S. at 100° F. and a viscosity index of 70 gave a flow–pressure curve

showing no yield value. With the addition of 1.25% of water based on the soap an immediate yield value of 44 gm. was obtained, and, on standing overnight, the reading rose to about 600 gm. This value was much greater than any obtained with the stearate, and for subsequent experiments it was necessary to cut down the soap concentration to 15%.

Further experiments showed that the use of an oil of lower viscosity index or a small amount of oleic acid with oils of higher viscosity index produced swelling in the soap. The swollen material behaved as a very viscous liquid and no yield value could be found. The addition of water to this viscous mass reduced the viscosity greatly and produced a high yield value. In some instances on the addition of an excess of water the soap became, with agitation, sufficiently lyophobic to give a yield value and viscosity very close to that of the original suspension prior to swelling. In these cases the attraction of the soap particles for one another was largely lost. The reason for this phenomenon is not at all clear, although it appears to be connected with the unsaturation of the acid radical, since it did not occur with the stearate.

Discussion

Microscopic examination of the dispersions of both calcium stearate and oleate after the addition of small quantities of water showed that considerable agglomeration had taken place. This is in agreement with results obtained in the measurement of sedimentation volumes of a number of substances in organic media, after the addition of small quantities of water (3, 4). The effect of other polar non-solvent addition agents, such as glycerol and fatty acid, is similar. It seems probable that after the adsorption of these substances on the polar groups of the calcium soaps, the surface properties are so altered that the attraction between particles of soap is now greater than the attraction between oil and soap, and flocculation takes place. There is thus set up in the system a structure that offers a finite resistance to distortion and gives rise to a yield value. Once this resistance has been overcome, however, the flow–pressure relation is linear. This increase in yield value would scarcely be expected if the increased sedimentation volume were due to the formation of lyospheres, as suggested by Ostwald and Haller (5). Similar results have been obtained with pigments in organic media (2). Since the viscosity of the oil is responsible for the slope of the flow–pressure curve, addition agents will have little effect on it unless they promote swelling.

Systems of this type, although prepared at room temperature with a rather poor dispersion of the soap, probably give a fairly accurate picture of certain steps in the process of grease manufacture. The finished product resembles a commercial grease in texture and appearance, although the consistency is much lower for a given soap content. Flow–pressure curves obtained with diluted commercial greases corroborate this conclusion.

Acknowledgment

This work was carried out under an arrangement between the Imperial Oil Limited and the National Research Council of Canada.

The authors wish to express their thanks to Imperial Oil Limited for permission to publish this paper.

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AN AUTOMATIC BURETTE FOR THE DELIVERY OF GAS AT CONSTANT PRESSURE[1]

By J. W. Hodgins[2] and R. B. Harvey[2]

Abstract

An apparatus has been built to control automatically the addition of gas, from a gas burette, to a system maintained at constant pressure. A phototube-relay, actuated by the mercury level of a manometer connected to the system, acts as the control mechanism for the gas input.

An apparatus has been built whereby known volumes of gas may be added to a system maintained at constant pressure. Taylor and Strother (3) have built a device to maintain a constant pressure in a system. A manometer operates a make and break contact that sets in action a gas electrolysis cell. In this case a fall in pressure causes electrolysis to proceed and restores the gas pressure in the system. Another type of pressure operated relay device has been described by Hoffmann (1) but his apparatus does not allow measurement of the volume of gas being added to the system. Recently Oliver and Bickford (2) published an article on a "Device for Electronic Control of Reduced Pressures" but this apparatus again uses a make and break contact system and a rubber valve. It was felt that any mechanical contact in the manometer or the reaction system should be avoided if possible and, for that reason, a photoelectric system with pressure control by means of interruption of a light beam was selected as the primary control. In Fig. 1 is shown a diagrammatic representation of the system in use.

The operation of the device can be followed by reference to Fig. 1. The bulb, *A*, acts as a reservoir between the burette and the reaction system. The manometer registers the pressure in the system and a stopcock is provided to allow re-evacuation of the zero pressure side of the manometer. The burette, *K*, from which gas is delivered to the system, has a three-way stopcock to allow filling of the burette from a source of supply of the gas, or discharge to the system. The mercury reservoir, *G*, has a flexible connection to permit variations in the mercury level in *G* and *K*. *F* is a pinchclamp operated by the solenoid, *E*, and *H* is a bubble trap to catch any entrained gas bubbles in the mercury. The light source and slit, *B*, are so adjusted that the light passes through the glass manometer arm and falls on the photocell, *C*.* The phototube was mounted at the end of a length of shielded cable to allow it to be moved easily in relation to the light source. The screw, *L*, allows small adjustments of the pressure to be made prior to operation. The light beam should be narrow and parallel to the plane of the mercury meniscus so that sensitivity will be maximum.

[1] *Manuscript received June 19, 1945.*
Contribution from the Chemical Warfare Laboratories, Ottawa, Canada.

[2] *Captain, Canadian Army.*

* *The phototube-relay system was described in an R.C.A. Bulletin entitled "Phototubes" (Fig. 5, page 10). Any of the numerous phototube-relays mentioned in the literature will serve.*

The action of the apparatus is as follows. With A isolated from the system by means of the stopcock, the bulb A, the manometer, and K are filled with gas at the desired pressure. The pressure is adjusted accurately and the light source levelled with L until the mercury meniscus just intercepts the beam falling on the photocell. The stopcock between A and the reaction system

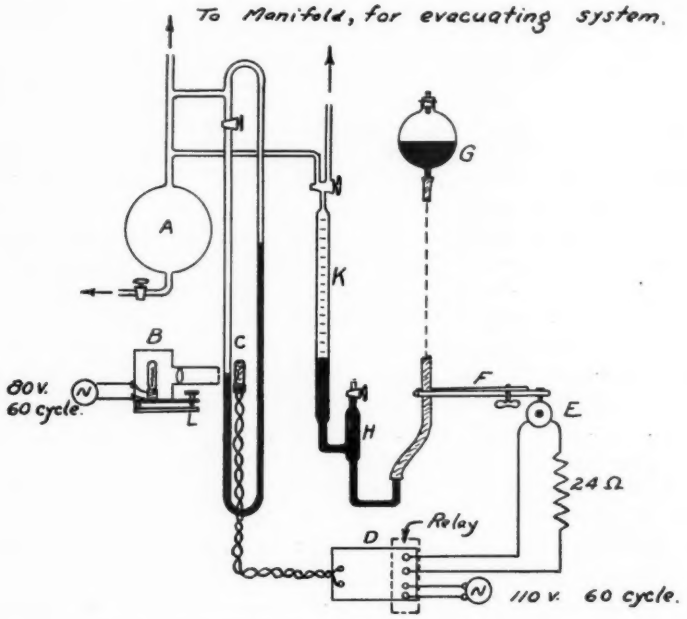

FIG. 1. *Assembly of phototube, manometer, and gas burette.*

is opened. Passage of gas out of A causes the level of the mercury in the closed manometer arm to fall. The mercury no longer intercepts the light beam falling on the phototube, and the relay is actuated. This causes the pinchclamp to be opened by the solenoid and mercury flows from G into K. Gas is displaced into the system and the pressure is restored.

Pressure regulation for periods of two hours is good to within ± 0.05 mm. For more accurate work it is necessary to insulate the gas-containing apparatus, as room temperature variations may cause the pressure to fluctuate seriously. Reaction pressures are changed simply and rapidly be displacing the light-source–phototube assembly vertically.

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A NOTE ON THE VISCOSITIES OF SOLUTIONS OF NITROCOTTON IN A MIXED NITROGLYCERINE-NITROGLYCOL SOLVENT[1]

By David Fensom[2]

Abstract

Viscosities of solutions of a number of types of nitrocotton in a mixed solvent consisting of 80% glyceryl trinitrate and 20% ethylene glycol dinitrate by weight have been measured in a modified Stormer viscometer. Complete solution was attained only with difficulty, but such solutions when obtained showed viscosity–concentration relations similar to those obtained with acetone solutions.

There is apparently no published information concerning the viscosity of solutions of the various types of nitrocotton in liquid nitric esters. A number of such measurements have recently been made for industrial purposes, and, although no high degree of accuracy is claimed, it is thought that the results may be of general scientific interest. The measurements cover a variety of grades of nitrocotton, made up into solutions in a low-freezing mixture containing 80% by weight nitroglycerine (glyceryl trinitrate) and 20% nitroglycol (ethylene glycol dinitrate).

Experimental Method

For the purpose of these experiments, a Stormer viscometer was modified by replacing the normal steel cup by one of bakelite. Since this cup was slightly conical, and, because of the unknown end effects, conditions of uniform shear were not exactly attained, and measurements of thixotropy (1) could not be made with accuracy. Such considerations were however found to be important only for solutions of the least degraded nitrocottons. The viscometer was calibrated with castor oil at 20° and 10° C., and water and glycerine–water solutions at 20° C., and it is considered that an accuracy of about 5% was normally attained in viscosity measurements.

The nitrocottons used were samples from normal manufacture, and were not specially purified or fractionated. The 80 : 20 nitroglycerine–nitroglycol mixture was also drawn from normal commercial production, and filtered immediately before use. More than one batch of solvent was used in the course of the work. An addition of 0.5% Ethyl Centralite (symmetrical diethyldiphenylurea) was made to the mixtures so that the latter could safely be heated to bring about complete solution of the nitrocotton.

The ingredients of each solution were weighed into an aluminum dish, stirred together for five minutes, and then heated at 60° C. until solution of the nitrocotton was as complete as possible. This was normally the case after about 18 hours, but it should be pointed out that in solutions of some of

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the highest viscosity nitrocottons, a small proportion of partially undissolved nitrocotton fibres could still be observed microscopically after the most prolonged heat treatment. After cooling, the solutions were brought to 20 ± 0.5° C. in the bakelite cups, and the viscosities measured at three or four rates of shear, beginning with the lowest. The results could be reproduced from different samples with a precision of about 10%, the variation apparently being due mainly to the difficulty of ensuring complete solution.

TABLE I

VISCOSITIES OF SOLUTIONS OF NITROCOTTONS IN 80 : 20 NITROGLYCERINE–NITROGLYCOL MIXTURE

Nitrocotton	Concentration, % wt.*	Time of heat treatment at 60° C., hr.	Applied load, gm.	Viscosity, centipoises†
	—	—	50	23.0
HX 3–5	2.00	20	300	86
	4.00	18	300	370
	6.00	18	300	1520
HX 8–13	1.00	18	150	48
	2.00	20	300	113
	4.00	20	300	950
	6.00	18	300	2000
HX 30–50	1.00	18	150	54
	2.00	18	300	181
	4.00	18	300	1260
HL 30–40	1.00	20	300	138
	2.00	20	300	1110
HL 120–170	0.50	18	300	135
	1.00	18	300	400
	2.00	20	300	2520
HM 15–20	0.50	20	300	94
	1.00	20	300	380
	2.00	20	300	4900
HH 5–15	0.50	18	150	150
			300	105
	1.00	18	150	2500
			300	1700
			600	1200
Blasting soluble	0.50	36	150	3050
			300	1670
			600	740
	1.00	36	300	9200
			600	6700
			900	3550

* *Grams per 100 gm. solution.*

† *Single determinations, recorded to three significant figures.*

Discussion of Results

Experimental results are recorded in Table I, whilst the properties of the nitrocottons used are given in Table II. For the sake of brevity, results at several rates of shears are recorded in Table I only, when the variation is greater than can be accounted for by experimental error; in other cases a single viscosity result is given, corresponding to a load of 300 gm., or the nearest load that was practicable experimentally.

TABLE II

PROPERTIES OF NITROCOTTONS USED IN PRESENT WORK

Nitrocotton	Raw material	N_2, %	Viscosity in 95% acetone*	
			Visc., poises	Solute, %
HX 3–5	Cotton linters	11.84	4	40
HX 8–13	" "	11.89	10	40
HX 30–50	" "	11.90	32	40
HL 30–40	" "	11.94	38	20
HL 120–170	" "	12.07	150	20
HM 15–20	" "	11.90	17	10
HH 5–15	" "	11.81	7	3
Blasting soluble	Cotton cops	12.26	140	4

* *Grams nitrocellulose per 100 ml. solvent, 95% by volume acetone, 5% water.*

TABLE III

EFFECT OF HEAT TREATMENT ON VISCOSITY

Solution: 6% HX 8–13 nitrocotton in nitroglycerine–nitroglycol mixture, with addition of 0.5% Ethyl Centralite

Temperature: 60° C.

Time of treatment, hr.	Viscosity, centipoises
1	1130
3	1370
18	1920
36	2120
72	1960
144	1840

A series of results is given in Table III to illustrate the effect of heat treatment on the viscosity of a 6% solution of HX 8–13 nitrocotton. Even at this high concentration, the sample heated for 18 hr. at 60° C., had reached maximum viscosity, thus justifying the adoption of 18 to 20 hr. as the normal maturing period for solutions.

Except at the highest viscosities, the results were in accordance with the empirical Arrhenius equation (3),

$$\eta/\eta^\circ = e^{kC},$$

where η and η° are the viscosities of the solution and pure solvent respectively in centipoises, C is the concentration of solute, in grams per 100 gm. solution, and k is a constant.

This is clear from Fig. 1, in which the logarithm of the viscosity is plotted over the concentration for several series of nitrocotton solutions. Straight lines were obtained with the nitrocottons of low viscosity, but at the higher

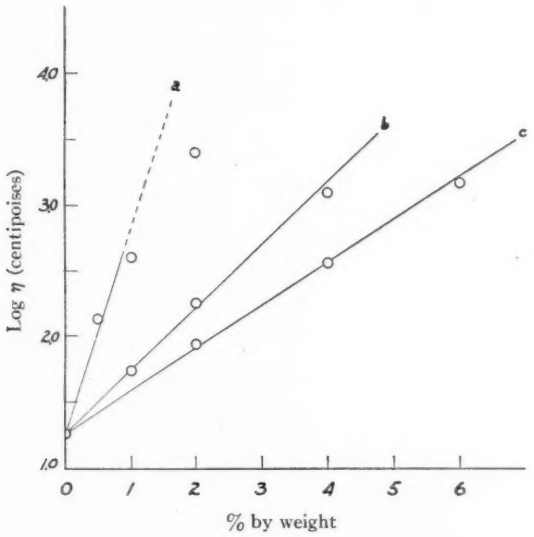

FIG. 1. *Viscosity–concentration curves for nitrocotton solutions. a = HL 120-170. b = HX 30-50. c = HX 3-5.*

concentrations of the less degraded nitrocottons the viscosity increase was less than that predicted by the equation. The experimental accuracy was thought to be insufficient to justify attempts to fit the data to more complicated equations.

Since dilute solutions of nitrocotton in acetone also obey the Arrhenius equation (3), it is of interest to compare the values of the constants k obtained with the same sample of nitrocotton in the two solvents. The graph, Fig. 2, shows the results. Within the experimental error, the values of k obtained with the nitroglycerine–nitroglycol mixture were 1.5 times those obtained with acetone as solvent. The lower values of k obtained in the latter case agree with the relatively higher solvent power of acetone for nitrocotton, the general trend agreeing with that to be expected from the results of work with other solvents (2, 3).

An apparent discrepancy occurs in the case of HH nitrocotton, for which an abnormally low value was obtained with the nitric ester solvent, but the thixotropy shown by solutions of this nitrocotton prevents a true application of the Arrhenius equation. Moreover this nitrocotton was especially difficult to dissolve completely in the nitroglycerine–nitroglycol mixture.

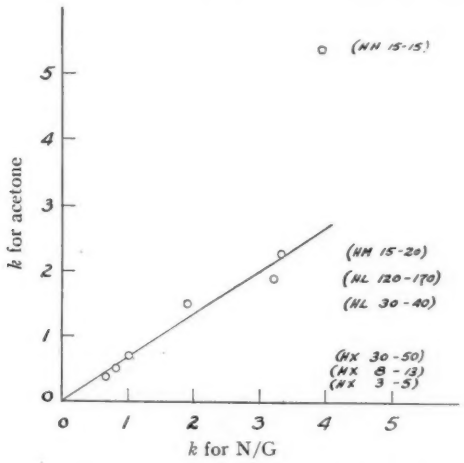

FIG. 2. *Arrhenius constants in acetone and liquid nitric ester.*

From the results obtained, therefore, it may be concluded that although it is difficult to obtain complete solution of nitrocotton in the low-freezing nitroglycerine mixture used in these experiments, yet such solutions when made exhibit viscosity–concentration relations similar to those of solutions of nitrocotton in acetone and other solvents.

Acknowledgment

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